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(54) **A heat sensitive imaging element and a method for producing lithographic plates therewith**

Wärmempfindliches Aufzeichnungselement und Verfahren zur Herstellung einer lithographischen Druckform damit

Elément d'enregistrement thermosensible et méthode pour la fabrication d'un cliché lithographique utilisant cet élément

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WO-A-97/00175

- **YOERGER W E ET AL: "REPELLENT COMPOSITION AND ELEMENTS CONTAINING THE SAME" RESEARCH DISCLOSURE,February 1974, pages 24-28, XP002019315**

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Description

Field of the invention.

[0001] The present invention relates to a method for making a heat sensitive recording material for making a lithographic printing plate precursor for use in lithographic printing without dampening.

Background of the invention.

[0002] Lithographic printing is the process of printing from specially prepared surfaces, some areas of which are capable of accepting ink (oleophilic areas) whereas other areas will not accept ink (oleophobic areas). The oleophilic areas form the printing areas while the oleophobic areas form the background areas.

[0003] Two basic types of lithographic printing plates are known. According to a first type, so called wet offset printing plates, both water or an aqueous dampening liquid and ink are applied to the plate surface that contains hydrophilic and hydrophobic areas. The hydrophilic areas will'be soaked with water or the dampening liquid and are thereby rendered oleophobic while the hydrophobic areas will accept the ink. A second type of lithographic offset printing plates operates without the use of a dampening liquid and are called driographic printing plates. This type of printing plates comprises highly ink repellant areas and oleophilic areas. Generally the highly ink repellant areas consist of a silicone layer.

[0004] Driographic printing plates can be prepared using a photographic material that is made image-wise receptive or repellant to ink upon photo-exposure of the photographic material. However heat sensitive recording materials, the surface of which can be made image-wise receptive or repellant to ink upon image-wise exposure to heat and/or subsequent development are also known for preparing driographic printing plates.

[0005] For example in DE-A-2512038 there is disclosed a heat sensitive recording material that comprises on a support carrying or having an oleophilic surface (i) a heat sensitive recording layer containing a self oxidizing binder e.g. nitrocellulose and a substance that is capable of converting radiation into heat e.g. carbon black and (ii) a non-hardened silicone layer as a surface layer. The disclosed heat sensitive recording material is image-wise exposed using a laser and is subsequently developed using a developing liquid that is capable of dissolving the silicone layer in the exposed areas. Subsequent to this development the silicone surface layer is cured. Due to the use of naphta as a developing liquid the process is ecologically disadvantageous. Further since the surface layer is not hardened the heat sensitive recording material may be easily damaged during handling.

[0006] FR-A-1.473.751 discloses a heat sensitive recording material comprising a substrate having an oleophilic surface, a layer containing nitrocellulose and carbon black and a silicone layer. After image-wise exposure using a laser the imaged areas are said to be rendered oleophilic. The silicone layer decomposed on the exposed areas is removed on press. Ink acceptance of the obtained plates is poor and the printing properties such as printing endurance and resolution of the copies is rather poor.

[0007] Research Disclosure 19201 of april 1980 discloses a heat sensitive recording material comprising a polyester film support provided with a bismuth layer as a heat sensitive recording layer and a silicon layer on top thereof. The disclosed heat sensitive recording material is imaged using an Argon laser and developed using hexane.

[0008] EP-A-573091 discloses a method for making a lithographic printing plate requiring a heat sensitive recording material comprising on a support having an oleophilic surface (i) a recording layer having a thickness of not more than 3µm and containing a substance capable of converting the laser beam radiation into heat and (ii) a cured oleophobic surface layer and wherein said recording layer and oleophobic surface layer may be the same layer. The exposed material is processed by a rub-off step.

[0009] GB-1 387 542 discloses the preparation of an electrophotographic toner image on a silicone layer. The toner image is thermally fused. There is no mention that the ink accepting phase is a continuous phase.

[0010] JP 63-22687 discloses a lithographic printing plate wherein on a support is coated a dispersion layer which contains particles comprising a thermoplastic resin containing fluorine and a binder resin, and a tetrafluoroethylene resin and a polymer of fluorine-containing acrylic acid are adapted to the particles of the thermoplastic resin containing fluorine. It is not disclosed that said binder is ink accepting.

[0011] US-P 4 010 687 discloses a printing master and a a method for producing the same which comprises: coating a suitable substrate with a layer of an ink releasable material selected from the group consisting of silicone elastomers and heterophase polymeric compositions. It is not mentioned that the non-silicone phase is a continuous phase.

[0012] US-P 4 686 138 discloses a printing plate for offset printing which comprises a water resistant support and an image receiving layer provided thereon which comprises an inorganic pigment and a mixed binder comprising a water-soluble high polymer compound and a synthetic high polymer latex. It is not mentioned that an inkabhesive phase is present.

[0013] WO 97/175 discloses a printing plat including a substrate, an IR absorbing layer comprised substantially of

a first water based emulsion and a top IR ablatable layer comprised substantially of a second water based emulsion. It is not disclosed that said top layer consist of two phases.

[0014] EP-A 755 803 discloses a lithographic printing plate comprising the non-image area of a hydrophilic swellable layer ; being 1 to 50 mg/m^2 in water absorbability, and the water absorbability of the image area, being less than that of the non-image area. It is not disclosed that said plate comprises an ink abhesive phase.

[0015] US-P 4 012 254 discloses a process for preparing a nonimage photoconductive waterless lithographic printing master comprising providing a heterogenous copolymer containing an abhesive species of polysiloxane groups and an imaging material adhesive species of organic thermoplastic groups, providing a solvent which will preferentially dissolve one of said species, placing said copolymer in said solvent wherein the non-soluble species forms micelles, providing a photoconductive pigment and dispersing said pigment in the resultant solution, providing a suitable master substrate and coating the resultant suspension on said master substrate, and allowing the solvent to evaporate whereby the soluble species forms the matrix in which the pigment is dispersed. It does not disclose the presence of a ink accepting homogeneous phase.

[0016] XP02019315 discloses a repellant composition for making driographic printing plates comprising a polysiloxane oil, a solid fluorinated polymer and a hydrophobic polymeric binder. However, the described composition is solvent coatable.

[0017] From the above it can be seen that a number of proposals have been made for making a driographic printing plate using a heat sensitive recording material. All these plates have the disadvantage that they have to be processed or that they are prepared by ablation. In both cases there originates waste in the preparation of said plates. A printing plate prepared by a really wasteless process remains an unanswered wish of the printing industry.

Summary of the invention.

[0018] It is an object of the present invention to provide a method for obtaining a driographic printing plate of high quality using a heat sensitive recording material that is prepared by a wasteless process.

[0019] Further objects of the present invention will become clear from the description hereinafter.

[0020] According to the present invention there is provided a method for making a lithographic printing plate precursor comprising the steps of:

- preparing an aqueous solution comprising an ink-accepting polymer latex and an ink-abhesive silicone latex in a ratio between 1:10 and 10:1
- coating the aqueous solution on a support, thereby obtaining an image-recording layer.

Detailed description of the invention.

[0021] It has been found that the above described heat sensitive recording material yields printing plates without a developing process or without waste, what results in an economical and an ecological benefit.

[0022] In the present invention a hydrophilic polymer means that water will adhere to said polymer when coated on a support and brought in contact with a mixture of water and oil. However a layer of such a hydrophilic polymer can adhere to oil when brought in contact with a waterless oily solution. Also in the present invention an oleophilic polymer means that oil will adhere to the polymer when coated on a support and brought in contact with a mixture of water and oil.

[0023] According to the present invention the ink accepting polymer comprises a latex of an oleophilic polymer. Specific examples of oleophilic polymer latices for use in connection with the present embodiment of the invention are preferably polyvinyl chloride, polyvinylidene chloride, polyacrylonitrile, polyvinyl carbazole etc., copolymers or mixtures thereof. Most preferably used are polystyrene, polymethyl-methacrylate or copolymers thereof Said polymer latex may be hardened.

[0024] According to this embodiment the ink abhesive polymer comprises also an ink abhesive latex of a silicone based polymer. The ratio between the amount of ink abhesive latex and oleophilic binder lies in the range between 1: 10 to 10:1, more preferably in the range between 1:5 to 5:1, most preferably in the range between 1:2 to 2:1.

[0025] This embodiment has the advantage that it can be coated from an aqueous dispersion.

[0026] The thickness of the recording layer ranges preferably from 0.2 to 25 µm, more preferably from 1 to 10 µm.

[0027] The weight average molecular weight of the ink accepting or ink abhesive polymers may range from 5,000 to 1,000,000g/mol.

[0028] The polymer latices may have a particle size from 0.01 µm to 50 µm, more preferably between 0.05 µm and 10 µm and most preferably between 0.05 µm and 2 µm.

[0029] The heat sensitive recording material preferably includes a compound capable of converting light to heat. The compound capable of converting light into heat can be present in a layer contiguous to the recording layer but is preferably present in the recording layer. Suitable compounds capable of converting light into heat are more preferably

infrared absorbing components although the wavelength of absorption is not of particular importance as long as the absorption of the compound used is in the wavelength range of the light source used for image-wise exposure. Particularly useful compounds are for example dyes and in particular infrared dyes, carbon black, metal carbides, borides, nitrides, carbonitrides, bronze-structured oxides and oxides structurally related to the bronze family but lacking the A component e.g. $WO_{2.9}$. It is also possible to use conductive polymer dispersions such as polypyrrole or polyaniline-based conductive polymer dispersions. It has been found that carbon black yields very good and favorable results.

[0030] The support of the heat sensitive recording material may be any support which is suitable for lithographic printing materials. Said support can be a layer having a hydrophilic or a hydrophobic surface such as a polymeric, a metallic or a glass layer.

[0031] According to one embodiment of the present invention, the lithographic base has a hydrophilic surface which favourably influences the adhesion of aqueous coated layers. A particularly preferred lithographic base having a hydrophilic surface is an electrochemically grained and anodised aluminum support. According to the present invention, an anodised aluminum support may be treated to improve the hydrophilic properties of its surface. For example, the aluminum support may be silicated by treating its surface with sodium silicate solution at elevated temperature, e.g. 95°C. Alternatively, a phosphate treatment may be applied which involves treating the aluminum oxide surface with a phosphate solution that may further contain an inorganic fluoride. Further, the aluminum oxide surface may be rinsed with a citric acid or citrate solution. This treatment may be carried out at room temperature or can be carried out at a slightly elevated temperature of about 30 to 50°C. A further interesting treatment involves rinsing the aluminum oxide surface with a bicarbonate solution. Still further, the aluminum oxide surface may be treated with polyvinylphosphonic acid, polyvinylmethylphosphonic acid, phosphoric acid esters of polyvinyl alcohol, polyvinylsulphonic acid, polyvinylbenzenesulphonic acid, sulphuric acid esters of polyvinyl alcohol, and acetals of polyvinyl alcohols formed by reaction with a sulphonated aliphatic aldehyde. It is further evident that one or more of these post treatments may be carried out alone or in combination.

[0032] The hydrophobic supports may be opaque or transparent, e.g. a paper support or a resin support. When a paper support is used preference is given to one coated at one or both sides with an alpha-olefin polymer, e.g. a polyethylene layer which optionally contains an anti-halation dye or pigment. Preferably an organic resin support is used e.g. cellulose esters such as cellulose acetate, cellulose propionate and cellulose butyrate; polyesters such as poly(ethylene terephthalate); polyvinyl acetals, polystyrene, polycarbonate; polyvinylchloride or poly-Alpha-olefins such as polyethylene or polypropylene.

[0033] One or more subbing layers may be coated between the support and the recording layer for use in accordance with the present invention in order to get an improved adhesion between these two layers.

[0034] In order to obtain a lithographic plate the heat sensitive element according to the invention is image-wise heated or exposed to actinic light and is then used as a printing plate without further development.

[0035] Heat is preferably applied by a thermal printer

[0036] Actinic light is light that is absorbed by the compound converting light into heat.

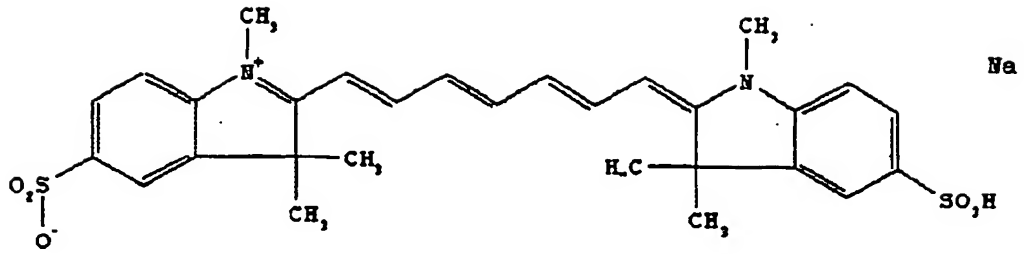
[0037] Image-wise exposure in connection with the present invention is preferably an image-wise scanning exposure involving the use of a laser or L.E.D.. It is highly preferred in connection with the present invention to use a laser emitting in the infrared (IR) and/or near-infrared, i.e. emitting in the wavelength range 700-1500nm. Particularly preferred for use in connection with the present invention are laser diodes emitting in the near-infrared.

[0038] According to the present invention depending on the amount of oleophilic latices in regard to the amount of ink abhesive latices the exposed areas become ink abhesive while the unexposed areas remain ink accepting or the exposed areas become ink accepting while the unexposed areas remain ink abhesive.

[0039] The following examples illustrate the present invention without limiting it thereto. All parts are by weight unless otherwise specified.

EXAMPLE 1

[0040] An aqueous dispersion is prepared by mixing 2.5 g of a 20% polystyrene dispersion with 4.0 g of a 50% silicone emulsion (Dehesive 410 E from Wacker-Chemie GmbH, Germany), 0.81 g of a 37% of a methyl hydrogen siloxane crosslinking agent (V 72 from Wacker-Chemie GmbH, Germany) and 0.12 g of an infrared absorbing dye with the following formula:



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[0041] The dispersion is made up with water to a total volume of 20 ml and well mixed. The dispersion is coated with a coating knife on a PET polyester support at a wet thickness of 20 µm and dried at a temperature of 60°C during 10 minutes.

[0042] An image is formed with an external drum diode laser (830 nm) with an output level of 305 mW and a drum-speed of 8 m/s.

The negative image material is used as a waterless printing plate on an AB DICK 9860 printing press using a Hostman-Steinberg Reflecta Dry ink (magenta). Up to 100 copies of the image were satisfactorily printed.

Claims

1. A method for making a heat-sensitive lithographic printing plate precursor comprising the steps of:
   - preparing an aqueous solution comprising an ink-accepting polymer latex and an ink-abhesive silicone latex in a ratio between 1:10 and 10:1
   - coating the aqueous solution on a support, thereby obtaining an image-recording layer.
2. Method according to claim 1 wherein the ink-accepting polymer latex is selected from the group of polystyrene, polymethylmethacrylate, polyvinyl chloride, polyvinylidene chloride polyacrylonitrile, polyvinylcarbazole, copolymers or mixtures thereof.
3. Method according to any of the preceding claims wherein the ink-accepting polymer latex and the ink-abhesive silicone latex are present in a ratio between 1:5 and 5:1.
4. Method according to any of the preceding claims wherein the ink-accepting polymer latex and the ink-abhesive silicone latex are present in a ratio between 1:2 and 2:1.
5. A method of making a driographic printing plate comprising the step of image-wise exposing to heat or IR-light a printing plate precursor obtained by the method of claim 1 to 4, thereby obtaining an image consisting of ink-accepting and ink-abhesive areas.

Patentansprüche

1. Ein durch die nachstehenden Schritte gekennzeichnetes Verfahren zur Herstellung eines wärmeempfindlichen lithografischen Druckplattenvorläufers :
   - Anfertigung einer wäßrigen Lösung, die einen farbanziehenden Polymerlatex und einen farbabstoßenden Silikonlatex in einem Verhältnis zwischen 1:10 und 10:1 enthält,
   - Auftrag der wäßrigen Lösung auf einen Träger, wobei eine Bildaufzeichnungsschicht erhalten wird.
2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, daß** der farbanziehende Polymerlatex aus der Gruppe bestehend aus Polystyrol, Polymethylmethacrylat, Polyvinylchlorid, Polyvinylidenchlorid, Polyacrylnitril, Polyvinylcarbazol und Copolymeren oder Gemischen derselben gewählt wird.
3. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** der farbanziehende Poly-

merlatex und der farbabstoßende Silikonlatex in einem Verhältnis zwischen 1:5 und 5:1 enthalten sind.

4. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** der farbanziehende Polymerlatex und der farbabstoßende Silikonlatex in einem Verhältnis zwischen 1:2 und 2:1 enthalten sind.

5. Verfahren zur Herstellung einer driografischen Druckplatte, wobei ein nach dem Verfahren von Anspruch 1 bis 4 hergestellter Druckplattenvorläufer bildmäßig mit Wärme beaufschlagt oder IR-Licht belichtet wird, wobei ein aus farbanziehenden und farbabstoßenden Bereichen zusammengesetztes Bild erhalten wird.

Revendications

1. Procédé de fabrication d'un précurseur de cliché d'impression lithographique thermosensible, comprenant les étapes consistant à :

   - préparer une solution aqueuse comprenant un latex polymère acceptant l'encre et un latex à base de silicone repoussant l'encre, dans le rapport entre 1 : 10 et 10 : 1 ;
   - couler la solution aqueuse sur un support pour ainsi obtenir une couche d'enregistrement d'image.

2. Procédé selon la revendication 1, dans lequel le latex polymère acceptant est choisi parmi le groupe comprenant le polystyrène, le polyméthacrylate de méthyle, le chlorure de polyvinyle, le chlorure de polyvinylidène, le polyacrylonitrile, le polyvinylcarbazole, des copolymères ou des mélanges desdits éléments.

3. Procédé selon l'une quelconque des revendications précédentes, dans lequel le latex polymère acceptant l'encre et le latex à base de silicone repoussant l'encre sont présents dans le rapport entre 1 : 5 et 5 : 1.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel le latex polymère acceptant l'encre et le latex à base de silicone repoussant l'encre sont présents dans le rapport entre 1 : 2 et 2 : 1.

5. Procédé de préparation de cliché d'impression driographique comprenant les étapes consistant à exposer en forme d'image à la chaleur ou de la lumière infrarouge un précurseur de cliché d'impression obtenu par le procédé selon la revendication 1 à 4, pour ainsi obtenir une image constituée par des zones acceptant l'encre et par des zones repoussant l'encre.